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REDUCTION PATHWAYS OF CYCLOOCTATETRAENE IRON
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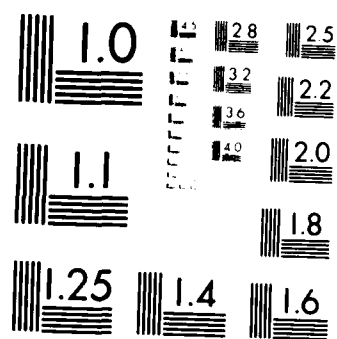
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Reduction Pathways of Cyclooctatetraene Iron Tricarbonyl
as Examined using Infrared Spectroelectrochemistry

by

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The nature of the redox-induced structural changes of cyclooctatetraene iron tricarbonyl are explored using fourier transform infrared spectroelectrochemistry. The results provide a simple demonstration of the detailed mechanistic information that can be obtained by employing FTIR instrumentation along with a thin-layer electrochemical arrangement.			
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Iron Tricarbonyl as Examined using Infrared Spectroelectrochemistry

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We have recently been examining the solvent-dependent electrochemical kinetics of several organometallic redox couples with the objective of gaining insight into the role of solvent reorganization dynamics on such simple electron-transfer processes.¹ One such system examined involves the electroreduction of tricarbonyl (η^4 -cyclo-octatetraene) iron(0) $[(COT)Fe(CO)_3]$.^{1b} In aprotic media this reactant undergoes two reversible one-electron reduction steps forming the mono- and diamines, respectively.^{2,3} In proton-containing solvents, however, the second step becomes chemically irreversible and merges into the first voltammetric wave.^{1b} In order to elucidate the nature of the redox-induced structural changes involved, we have examined the corresponding alterations in the vibrational spectra as deduced by using thin-layer FTIR spectroelectrochemistry. Pertinent results obtained in typical aprotic and protic media, acetonitrile and methanol, respectively, are reported in the present communication.

Details of the thin-layer spectroelectrochemical arrangement are given in ref. 4. The FTIR spectrometer was a Bruker/IBM Model 98-4A, with an MCT narrow-band detector. Each spectrum was acquired using 32 interferometer scans, requiring about 25 s. The thin-layer arrangement employed a modified Perkin-Elmer infrared solution cell, having a path length of 0.2 mm with a gold minigrid working electrode (100 wires/in, Buckbee-Mears), a platinum foil counter electrode and a Ag/AgCl reference electrode. All potentials are, however, quoted here versus the saturated calomel electrode (SCE). A PAR Model 173/175/179 potentiostat system was used for voltammetric measurements and thin-layer electrolyses.

Cyclooctatetraene iron tricarbonyl was synthesised as described in

ref. 9a. Acetonitrile and methanol (Burdick and Jackson) were distilled over calcium hydride and activated magnesium turnings, respectively.

Typical cyclic voltammograms for the reduction and reoxidation of 1.5mM (COT)Fe(CO)₃ in acetonitrile and methanol at a hanging mercury drop electrode are shown in Figs. 1A and B, respectively. The supporting electrolytes were 0.5M tetrabutylammonium hexafluorophosphate (TBAH) and tetrabutylammonium tetrafluoroborate (TBAB) in these two solvents. In acetonitrile (Fig. 1A), a pair of one-electron reduction waves are observed. While the first wave exhibits complete chemical reversibility even at slow sweep rates, the second (more negative potential) wave yielded reversible behavior (cathodic to anodic peak current ratio $i_c/i_a > 0.8$) only for sweep rates $\nu \geq 0.5 \text{ V s}^{-1}$. In methanol (Fig. 1B), a single voltammetric reduction wave is obtained; a significant anodic return wave became discernible only when using scan rates above ca. 50 V s^{-1} . The corresponding d.c. polarograms in acetonitrile yielded a pair of reduction waves with half-wave potentials, $E_{1/2}$, of -1.34 V and -1.53 V vs. SCE, having an amplitude and shape consistent with one-electron steps. A single two-electron wave, with $E_{1/2} \approx -1.39 \text{ V}$, was observed in methanol.

Infrared spectra were obtained for these systems before and after bulk electrolysis at a series of negative potentials using the thin-layer arrangement. Complete electrolysis in this cell, judged by the current falling below 2% of its initial value, generally required less than 30 s. A pair of FTIR spectra in the $1500\text{--}2200 \text{ cm}^{-1}$ region, obtained sequentially at potentials (-0.5 V and -1.5 V) in acetonitrile at which (COT)Fe(CO)₃ and the one-electron reduction product are present, are shown in Figs. 2A and B, respectively. The spectra are both referenced to a corresponding

reactant-free spectrum; the $(\text{COT})\text{Fe}(\text{CO})_3$ concentration is 5 mM.

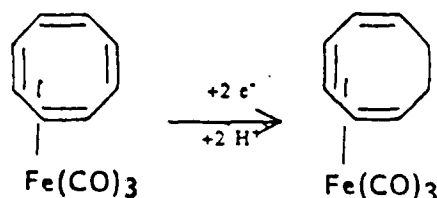
The most intense spectral features observed for $(\text{COT})\text{Fe}(\text{CO})_3$ are a pair of bands at 1980 and 2050 cm^{-1} , ascribed to C=O stretching modes, ν_{CO} . A detailed vibrational analysis of $(\text{COT})\text{Fe}(\text{CO})_3$ has identified three ν_{CO} modes in this frequency region;⁶ the pair of vibrations reported at 1976 and 1993 cm^{-1} in ref. 6 apparently remain unresolved within the broader band around 1980 cm^{-1} in the present spectra. Upon reduction to $(\text{COT})\text{Fe}(\text{CO})_3^-$, these bands are both shifted substantially to lower frequencies, 1890 and 1940 cm^{-1} (Fig. 2B). These changes are consistent with the added electron having significant metal-based character, the lower ν_{CO} frequencies arising from increased metal-carbonyl back bonding.⁷ The original spectrum (Fig. 2A) was reestablished upon returning the potential to -0.5 V, demonstrating the chemical reversibility of this one-electron step over the timescale (1-2 mins) required for these potential-dependent spectral measurements. However, upon further reduction, at a potential (-2.0 V) where the second one-electron step occurs (Fig. 1A), these spectral features disappeared irreversibly and bubbles became visible in the thin-layer cell, indicating decomposition of the carbonyl complex.

Figure 3 shows the corresponding spectral changes induced upon reduction of $(\text{COT})\text{Fe}(\text{CO})_3$ in methanol. Spectrum A was obtained at -0.5 V, and spectrum B after altering the potential to -1.5 V where the two-electron reduction proceeds (Fig. 1B). In contrast to Fig. 2, only a small (ca. 10 cm^{-1}) downshift of the ν_{CO} frequencies is observed upon reduction in methanol. This is indicative that there is only a small increase in electron density in the $-\text{Fe}(\text{CO})_3$ moiety brought about electroreduction. No further spectral changes were observed upon returning the potential to the

initial value, consistent with the electrochemical irreversibility of this system.

Although the spectral features associated with the COT ligand were weaker and less readily assigned, significant alterations in the 1200-1800 cm^{-1} region were seen upon electroreduction of $(\text{COT})\text{Fe}(\text{CO})_3$ in methanol. Most prominently, a new band at 1670 cm^{-1} appears (Fig. 3B) which is absent either for the starting material or upon electroreduction in acetonitrile (Fig. 2B). This feature is tentatively ascribed to a C-C stretching vibration. The higher frequency of this band with respect to several vibrations seen for $(\text{COT})\text{Fe}(\text{CO})_3$ around 1450-1550 cm^{-1} is suggestive of a loss of conjugation of the COT ring, yielding more localized C-C vibrations.

These observations are consistent with a concerted two-electron reduction occurring on the COT ring along with the addition of two protons:



with the $\text{Fe}(\text{CO})_3$ moiety remaining essentially unaffected and η^4 -bonded to the COT ligand. Such a product, involving protonation of adjacent ring carbons, has been isolated from the reduction of $(\text{COT})\text{Fe}(\text{CO})_3$ by potassium and the subsequent addition of water.³ The infrared spectrum for this species contains similar features to those in Fig. 3B, including a band around 1670 cm^{-1} .⁸

The present results therefore indicate that while the reversible reduction of $(\text{COT})\text{Fe}(\text{CO})_3$ in aprotic solvents involves significant metal-

centered character, the irreversible reduction observed in protic media is localized within the COT ring. The latter is, of course, consistent with hydrogenation of one of the C-C double bonds. While ESR spectroscopy of $(\text{COT})\text{Fe}(\text{CO})_3^-$ formed in aprotic media suggests that this reduction involves the COT ring,⁹ the present infrared evidence indicates that the electron is also delocalized significantly onto the $-\text{Fe}(\text{CO})_3$ moiety.

While making further structural inferences would require a substantially more detailed study than presented here, these results provide a simple demonstration of the redox mechanistic information that can be obtained relatively rapidly by employing FTIR instrumentation along with a thin-layer electrochemical arrangement.¹⁰

Acknowledgments

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Figure Captions

Fig. 1

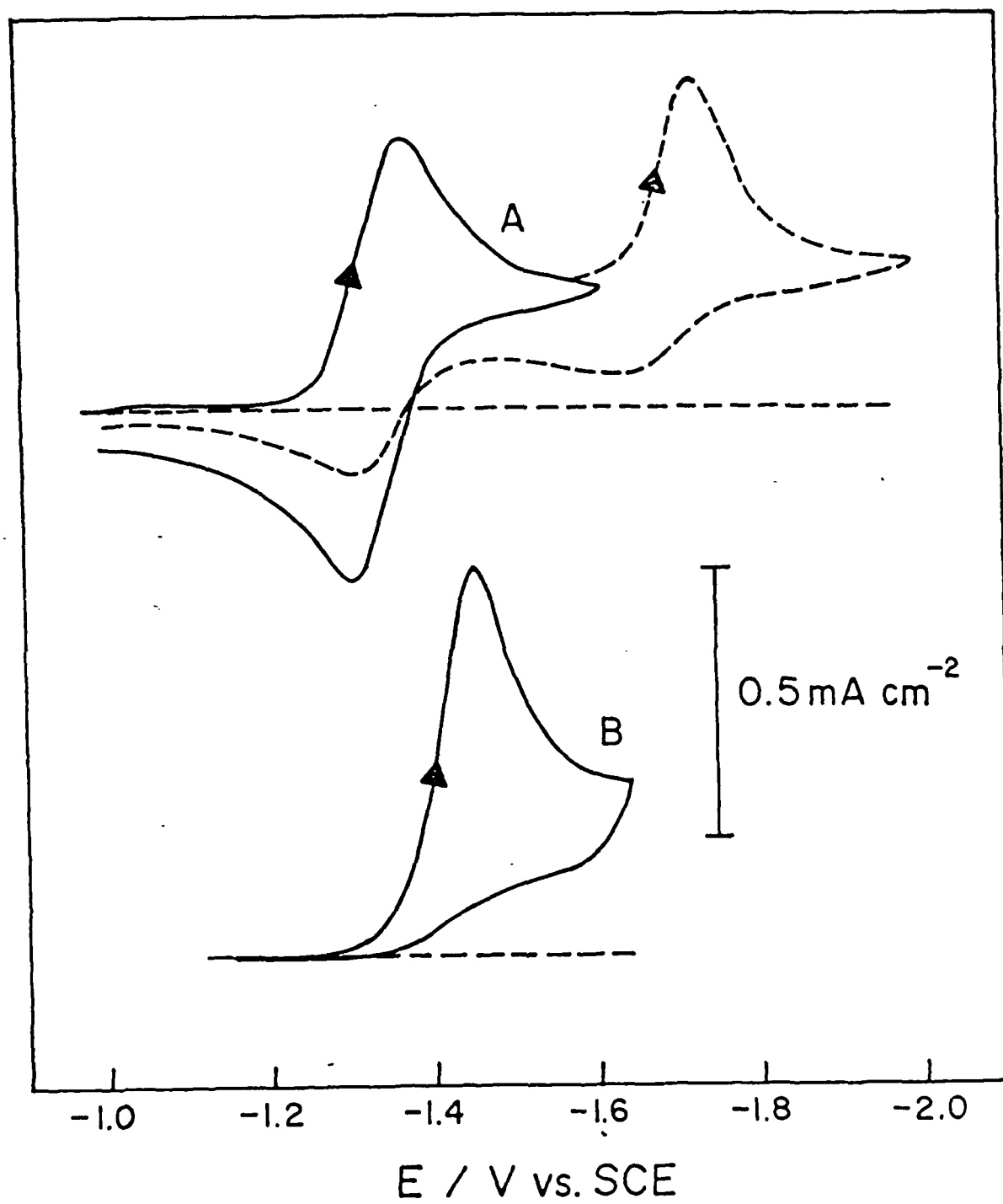
Cathodic-anodic cyclic voltammograms for $(\text{COT})\text{Fe}(\text{CO})_3$ at 0.2 V s^{-1} in (A) acetonitrile and (B) methanol using a hanging mercury drop electrode. Solutions contained 1.5 mM $(\text{COT})\text{Fe}(\text{CO})_3$ and 0.5 M TBAH and 0.5 M TBAB in A and B, respectively.

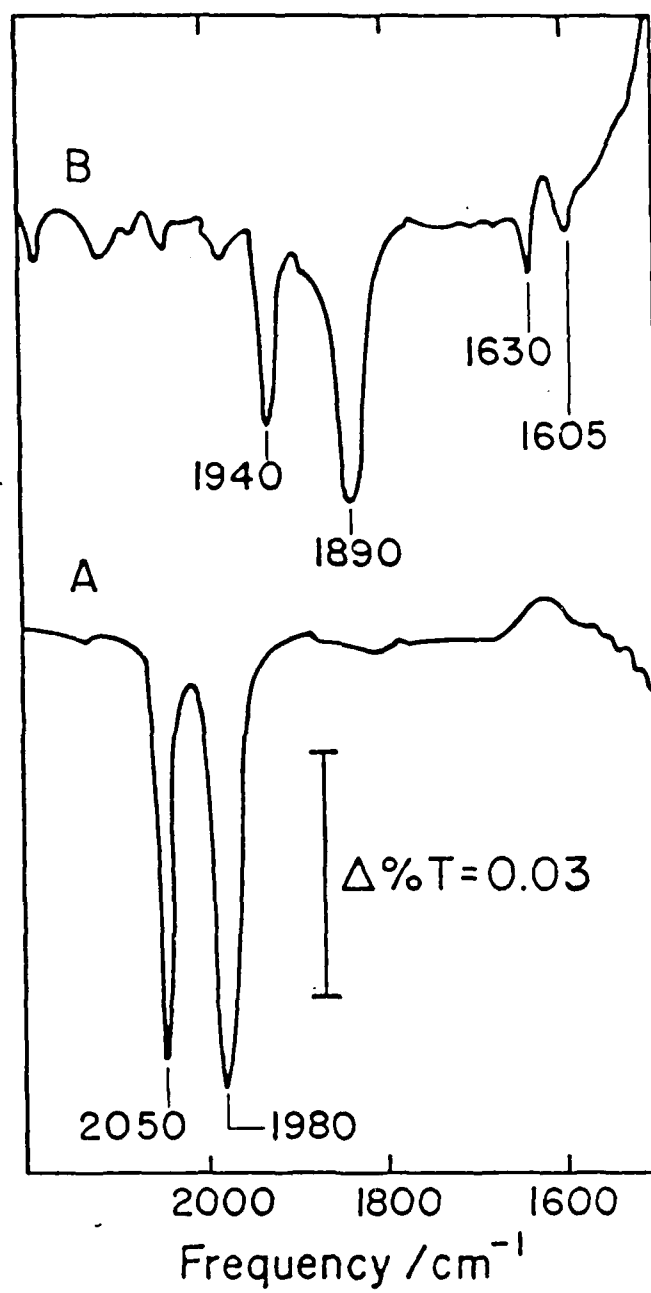
Fig. 2

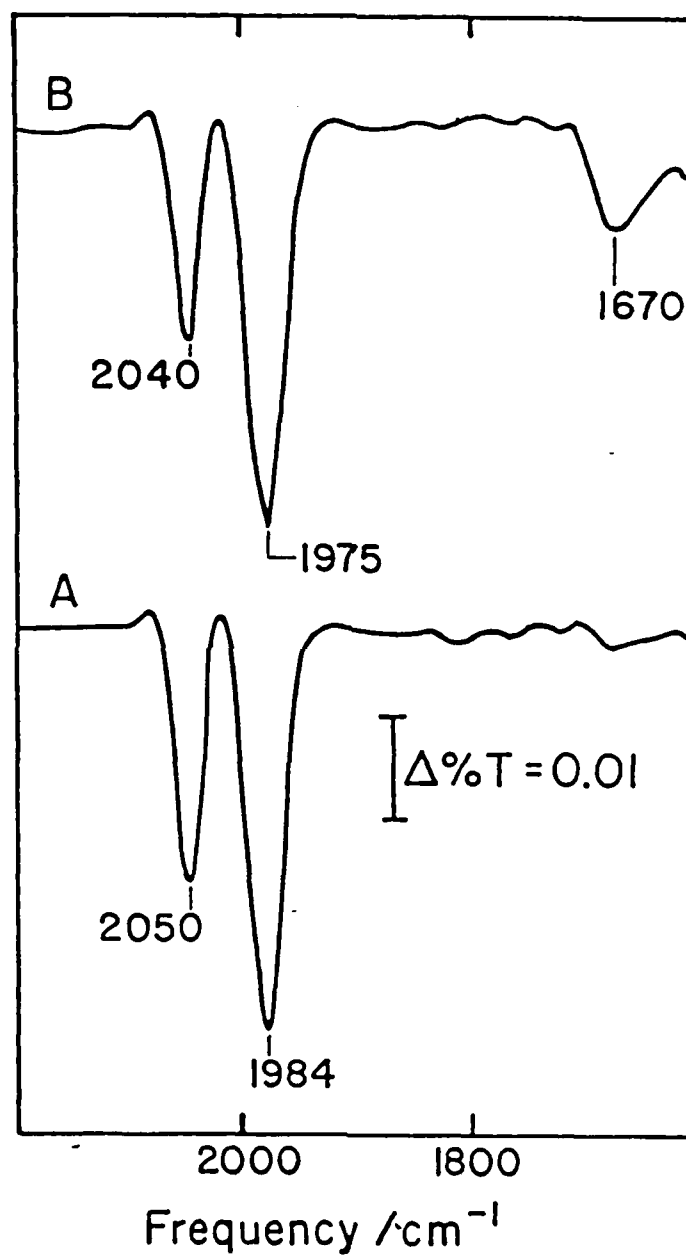
Transmittance infrared spectra for 5 mM $(\text{COT})\text{Fe}(\text{CO})_3$ in acetonitrile containing 0.5 M TBAH in $1500\text{-}2200 \text{ cm}^{-1}$ region (A) at -0.5 V vs. SCE, and (B) after electrolysis at -1.5 V . Spectra obtained in thin-layer electrolysis cell using 32 interferometer scans (acquisition time ca. 25 s), and referenced to a prior spectrum obtained in the absence of the reactant.

Fig. 3

Transmittance infrared spectra for 5 mM $(\text{COT})\text{Fe}(\text{CO})_3$ in methanol containing 0.5 M TBAB in $1600\text{-}2200 \text{ cm}^{-1}$ region (A) at -0.5 V and (B) after electrolysis at -1.5 V . For other details see caption to Fig. 2 and the text.







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